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H₂CAP - Hydrogen assisted catalytic biomass pyrolysis for green fuels

Magnus Zingler Stummann¹, Martin Høj¹, Jostein Gabrielsen², Peter Arendt Jensen¹, Anker Degn Jensen^{1*}

¹DTU Chemical Engineering, Technical University of Denmark, 2800 Kgs. Lyngby (Denmark)

²Haldor Topsøe A/S, 2800 Kgs. Lyngby (Denmark)

*aj@kt.dtu.dk

Introduction

Fast pyrolysis of biomass produces a high yield of bio-oil through well-established technologies [1]. To utilize this oil as liquid fuel the oxygen content must be reduced from 15-30 wt.% down to <1 wt.%, which increases heating value and stability and decreases acidity [1]. Upgrading bio-oil by catalytic hydrodeoxygenation (HDO) is challenged by severe polymerization and coking upon heating the oil. Alternatively, performing fast pyrolysis in high-pressure hydrogen atmosphere in a fluid bed reactor with a HDO catalyst as bed medium could immediately stabilize reactive pyrolysis vapors [2]. An additional vapor phase HDO reactor ensures removal of oxygen down to <1 wt%, resulting in separate hydrocarbon oil and water phases being recovered. A schematic diagram for such a process is shown in Figure 1. A simplified bench scale setup has been constructed at DTU Chemical Engineering. With a capacity of 100 to 300 g/h solid biomass, the aim is to provide a proof-of-concept for the continuous conversion of solid biomass to low oxygen, fuel-grade bio-oil.

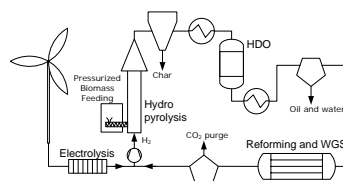


Figure 1: Simplified H₂CAP process diagram including fluid bed catalytic hydropyrolysis (20 to 40 bar and 350 to 500°C), char separation, temperature adjustment, vapor phase HDO reactor (20 to 40 bar and 300 to 400°C), cooling, condensation and liquid separation. These parts have been constructed at DTU Chemical Engineering. Additionally, steam reforming and water gas shift (WGS) of non-condensable gasses to H₂ and CO₂ and wind-powered electrolysis of water to H₂ is envisioned.

Materials and Methods

Experiments have been performed using 50 g of CoMo/MgAl₂O₄ catalyst in the fluid bed reactor and 173 g of NiMo/Al₂O₃ catalyst in the HDO reactor. The catalysts were sulfided at 25 bar with 2-7.5 % of H₂S, 5 % N₂ in balance H₂ by feeding liquid DMDS to the system. The hydropyrolysis of biomass have been performed at 25 bar with gas composition 470 ppm H₂S, 6 % N₂ balance H₂ at a total flow of 87 NL/min. The actual total flow at reaction temperature and pressure corresponds to approximately three times the minimum fluidization velocity (3u_{mf}) for the employed catalyst sieve fraction. The biomass used was beech wood, bark free and approximate particle size 200 to 700 µm. Moisture 5.75 wt.% (bone dry at 102 °C) and ash content 0.58 wt.% (dry basis).

Table 1: Reaction conditions employed in the first four experiments

	Exp. #1	Exp. #2	Exp. #3	Exp. #4
Biomass feed rate [g/min]	282	194	212	233
Feed time [min]	210	156	245	241
Fluid bed Temp. [°C]	425	400	400	470
Filter Temp. [°C]	340	335	330	340
HDO Temp. [°C]	375	350	400	390

Table 1 summarizes the reaction conditions in the four experiments performed so far. For each experiment a fresh load of catalyst in the fluid bed reactor and the same load of catalyst in the HDO reactor was used, but both catalyst were sulfided before each experiment.

Results and Discussion

A photograph of the condensed liquids from Exp. #4 and the yields obtained from Exp. #1 to #4 are shown in Figure 2.

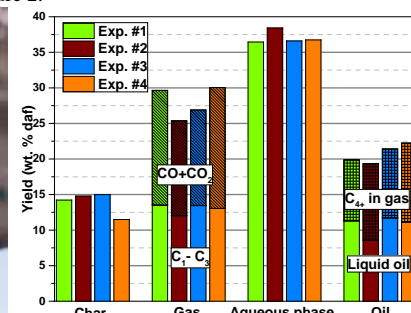


Figure 2: Photograph of recovered liquid from Exp. #4, oil is top phase. Yields of char, C₁-C₃ hydrocarbons, CO+CO₂, condensed aqueous phase and condensed oil with potentially condensed oil (C₄+) in gas phase on dry, ash free basis for Exp. #1 to #5. The mass balances sum to 100 %, 98 %, 100 %, 101 % and 91 % respectively.

The products are phase separated aqueous and hydrocarbon fractions. The produced oil has low viscosity, is free flowing, transparent and very different from conventional wood pyrolysis oil. The best oil yield is 22.2 wt.% of the wood, corresponding to approximately 39 % carbon atom yield and an energy yield of approximately 53 %. The oxygen content of the condensed oil has been measured to <1 wt.%, the hydrogen content approximately 12 wt.% and the carbon content approximately 88 wt.%, showing that the oil is hydrocarbons. Simulated distillation (SimDist by GC) showed that approximately 25 vol.% of the condensed oil is gasoline and 75 vol.% diesel. The main oxygenates left in the oil are 4-ethylphenol, dimethylphenol, benzofuran, dibenzofuran, methylbenzofurans and 2-naphthol, some of the least reactive compounds in HDO, as measured with O-specific GC-AED.

These very first results show that the process performs excellently as intended. The liquid yield may be further improved by choice of catalysts and reaction conditions, which is the focus of ongoing work.

Significance

This study confirms that catalytic hydropyrolysis with hydrodeoxygenation is an attractive route for biomass to liquid fuels. The reaction conditions employed are significantly milder than gasification, potentially resulting in lower capital and operating costs, and the energy yield is significantly better than second-generation bio-ethanol. The oil yields are comparable to those reported in literature [2,3].

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